Non-entropic theory of rubber elasticity: flexible chains with weak excluded-volume interactions

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Abstract

Strain energy density is calculated for a network of flexible chains with weak excluded-volume interactions (whose energy is small compared with thermal energy). Constitutive equations are developed for an incompressible network of chains with segment interactions at finite deformations. These relations are applied to the study of uniaxial and equi-biaxial tension (compression), where the stress–strain diagrams are analyzed numerically. It is demonstrated that intra-chain interactions (i) cause an increase in the Young's modulus of the network and (ii) induce the growth of stresses (compared to an appropriate network of Gaussian chains), which becomes substantial at relatively large elongation ratios. The effect of excluded-volume interactions on the elastic response strongly depends on the deformation mode, in particular, it is more pronounced at equi-biaxial tension than at uniaxial elongation.

Key-words: Flexible chain, Excluded-volume interaction, Polymer network, Finite deformation, Path integral

1 Introduction

This study is concerned with the elastic response of polymer networks at finite strains. According to the classical theory of rubber elasticity [1], an arbitrary chain in a network is treated as Gaussian, which allows a simple formula to be derived for the strain energy density of a network, and stress–strain relations to be developed in the analytical form. Two shortcomings of the concept of Gaussian chains are traditionally emphasized: (i) this model does not account for long-range interactions between segments (Gaussian chains can intersect themselves), and (ii) the end-to-end distance of a Gaussian chain exceeds its contour length with a non-zero probability. To avoid these disadvantages, it seems enticing to replace Gaussian chains in a network by flexible chains with excluded-volume interactions (this model does not permit self-intersections) or by semi-flexible chains (this approach guarantees that the end-to-end distance of a chain is always less than its contour length). Although the necessity to go beyond Gaussian chains has been realized for a long time (the seminal paper by Flory [2] appeared more than half a century ago), our knowledge of the mechanical behavior of networks of non-Gaussian chains remains rather limited, due to some

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difficulties in their mathematical treatment. Serious progress in the analysis of statistics of single polymer chains and membranes with excluded-volume interactions was reached by using the renormalization group technique [3, 4, 5, 6]. These methods, however, have been employed for the analysis of the distribution functions only and have not yet been applied to determine the strain energy of a network, despite the importance of the latter problem for applications, see [7, 8] and the references therein, as well as recent publications [9, 10, 11, 12].

This study is motivated by a problem which, at first glance, appears to be quite simple. Consider an incompressible permanent network of Gaussian chains with a given set of parameters (segment length b_0, contour length L, number of chains per unit volume M) at a fixed absolute temperature T. Suppose that Gaussian chains in the network are replaced by flexible chains (with the same parameters b_0, L and M) with excluded-volume interactions (whose strength v_0 will be defined later). The question is how the presence of intra-chain interactions affects the Young's modulus E of the network? In a more general context, this question may be reformulated as what is the influence of segment interactions on the stress–strain relations for the network?

In order to shed some light on this issue, it is necessary to define unambiguously what flexible chains with excluded-volume interactions mean. Two approaches are conventionally employed to describe configurations of a polymer chain. According to the first, a chain is thought of as a random walk with a small step length b_0 and a large number of steps N (their product $L = Nb_0$ is assumed to be finite when $N \to \infty$). Excluded-volume interactions between segments are treated as a constraint that rules out trajectories that intersect themselves (self-avoiding random walks), which implies that the "strength" of segment interactions v_0 has no physical meaning. A disadvantage of this concept is that the distribution function for end-to-end vectors $\mathbf{Q}$ of self-avoiding chains is unknown. Some approximations for this function are available at $\mathbf{Q} \to \infty$ [7], but they are insufficient for the determination of elastic moduli. Nevertheless, the effect of intra-chain interactions on the elastic moduli may be assessed qualitatively: as the number of configurations for a self-avoiding walk is lower than that for a walk without constraints, and the free energy of a chain is proportional to its entropy (which, in turn, is proportional to the logarithm of the number of available configurations), it is plausible to assume that excluded-volume interactions between segments reduce the stiffness.

According to the other approach, a chain is treated as a curve with length L in a three-dimensional space. Any configuration of the chain is described by the equation $\mathbf{r} = \mathbf{r}(s)$, where $\mathbf{r}$ stands for the radius vector, and $s \in [0, L]$. This configuration is characterized by a weight (energy), which is determined by some Hamiltonian $H(\mathbf{r})$. For a Gaussian chain, the Hamiltonian reads

$$H_0(\mathbf{r}) = \frac{3k_{\rm B}T}{2b_0} \int_0^L \Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2 ds, \tag{1}$$

while for a chain with excluded-volume interactions, this functional is given by [13]

$$H(\mathbf{r}) = H_0(\mathbf{r}) + \Phi(\mathbf{r}) \tag{2}$$

with

$$\Phi(\mathbf{r}) = \frac{v_0}{2L^2} \int_0^L \int_0^L \delta\Big(\mathbf{r}(s) - \mathbf{r}(s')\Big) ds ds'. \tag{3}$$

Here k_B is Boltzmann's constant, $\delta(\mathbf{r})$ denotes the Dirac delta-function, and the pre-factor v_0 characterizes strength of segment interactions.

Unlike the concept of random walks, an assessment of the influence of segment interactions on the Young's modulus E becomes non-trivial in this case. On the one hand, the presence of the second term on the right-hand side on Eq. (2) reduces the number of configurations with a noticeable weight, which results in a decrease in the free energy. On the other hand, this term

increases the energy H of any available configuration, which causes the growth of the average energy of a chain, and, as a consequence, an increase in the strain energy density of a network.

A rigorous treatment of the interplay between these two factors is the objective of this paper. Due to some technical difficulties in the evaluation of path integrals for the Hamiltonians (2) and (3), we confine ourselves to the analysis of weak excluded-volume interactions, whose energy $\Phi(\mathbf{r})$ is small compared with thermal energy $k_B T$.

The exposition is organized as follows. Section 2 deals with the free energy of a flexible chain and the strain energy density of a permanent network of polymer chains calculated within the entropic and non-entropic concepts. The free energy of a flexible chain with a small, but arbitrary functional $\Phi(\mathbf{r})$ is found in Section 3 in terms of an appropriate correlation function. Section 4 has a merely technical character. We derive some explicit expressions for correlation functions, which are employed in Section 5 to determine the free energy of a chain with excluded-volume interactions. Constitutive equations for a network of chains with weak segment interactions are developed in Section 6, where they are applied to the analysis of uniaxial and equi-biaxial tension of an incompressible medium. Some concluding remarks are formulated in Section 7.

2 The concept of non-entropic elasticity

We begin with a brief exposition of the classical theory of rubber elasticity [1], demonstrate its shortcomings, and introduce some refinement of the conventional approach. The concept of entropic elasticity is grounded on the treatment of a polymer chain as a random walk in a three-dimensional space. For definiteness, we suppose that the walk begins at the origin and has a fixed length b_0 of each step. The main hypothesis of this theory is that the distribution function $p(\mathbf{Q})$ of end-to-end vectors $\mathbf{Q}$ entirely describes configurations of a chain. The free energy of a chain $\Psi(\mathbf{Q})$ is connected with the distribution function $p(\mathbf{Q})$ by the Boltzmann equation

$$p(\mathbf{Q}) = \exp\Big(-\frac{\Psi(\mathbf{Q})}{k_B T}\Big). \tag{4}$$

In the nonlinear elasticity theory, two states of a medium are distinguished: (i) the reference (initial) state occupied before application of external loads, and (ii) the actual (deformed) state that is acquired after deformation. As a polymer chain is entirely characterized by the relative positions of its end-points, two vectors are introduced: the end-to-end vector in the reference state $\mathbf{Q}$, and that in the actual state $\mathbf{Q}'$. These quantities obey the equality

$$\mathbf{Q}' = \mathbf{F} \cdot \mathbf{Q}, \tag{5}$$

where $\mathbf{F}$ is a deformation gradient, and the dot stands for inner product. It follows from Eqs. (4) and (5) that the increment of free energy

$$\Delta\Psi(\mathbf{F},\mathbf{Q}) = \Psi(\mathbf{Q}') - \Psi(\mathbf{Q})$$

driven by deformation of the chain reads

$$\Delta\Psi(\mathbf{F},\mathbf{Q}) = k_B T\Big[\ln p(\mathbf{Q}) - \ln p(\mathbf{F}\cdot\mathbf{Q})\Big].$$

The strain energy per chain $W(\mathbf{F})$ is determined by averaging the increment of free energy over the initial distribution of end-to-end vectors,

$$W(\mathbf{F}) = k_B T \int \Big[\ln p(\mathbf{Q}) - \ln p(\mathbf{F}\cdot\mathbf{Q})\Big] p(\mathbf{Q}) d\mathbf{Q}, \tag{6}$$

where the integration is performed over the entire space. Given a strain energy W, stress–strain relations for a chain are determined by conventional formulas, see, e.g., [14]. Equation (6) is noticeably simplified when the distribution function $p(\mathbf{Q})$ is isotropic:

$$p(\mathbf{Q}) = p_*(Q), \qquad Q = |\mathbf{Q}|.$$

Bearing in mind that $|\mathbf{F}\cdot\mathbf{Q}| = (\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q})^{\frac{1}{2}}$, where

$$\mathbf{C} = \mathbf{F}^{\top}\cdot\mathbf{F}$$

is the right Cauchy-Green deformation tensor, and $\top$ stands for transpose, and introducing a spherical coordinate frame $\{Q, \phi, \theta\}$, we find that

$$W(\mathbf{C}) = k_B T\int_0^{\infty} p_*(Q)Q^2 dQ\int_0^{2\pi} d\phi\int_0^{\pi}\Big[\ln p_*(Q) - \ln p_*\Big((\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q})^{\frac{1}{2}}\Big)\Big]\sin\theta d\theta. \tag{7}$$

In particular, for a Gaussian chain with the radial distribution function

$$p_*(Q) = \Big(\frac{3}{2\pi b^2}\Big)^{\frac{3}{2}}\exp\Big(-\frac{3Q^2}{2b^2}\Big), \tag{8}$$

where $b = \sqrt{b_0 L}$ is the mean square end-to-end distance, Eq. (7) implies the classical formula

$$W(\mathbf{C}) = \frac{1}{2}k_B T\Big(\mathcal{I}_1(\mathbf{C}) - 3\Big), \tag{9}$$

where $\mathcal{I}_m$ stands for the mth principal invariant of a tensor.

According to the other way of modeling a polymer chain [13], each configuration is associated with a curve $\mathbf{r}(s)$ in a three-dimensional space. For a chain that begins at the origin and finishes at a point $\mathbf{Q}$, the radius vector $\mathbf{r}(s)$ satisfies the boundary conditions

$$\mathbf{r}(0) = \mathbf{0}, \qquad \mathbf{r}(L) = \mathbf{Q}. \tag{10}$$

The Green function (propagator) of a chain whose energy is described by a Hamiltonian $H(\mathbf{r})$ reads

$$G(\mathbf{Q}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\exp\Big(-\frac{H(\mathbf{r}(s))}{k_{\rm B}T}\Big)\mathcal{D}[\mathbf{r}(s)], \tag{11}$$

where the path integral with the measure $\mathcal{D}[\mathbf{r}]$ is calculated over all curves $\mathbf{r}(s)$ that obey Eq. (10). As the functional integral is determined up to an arbitrary multiplier [15], the additional restriction is imposed on the function $G(\mathbf{Q})$,

$$\int G(\mathbf{Q})d\mathbf{Q} = 1, \tag{12}$$

which ensures that the Green function $G(\mathbf{Q})$ coincides with the distribution function of end-to-end vectors $p(\mathbf{Q})$.

Within the entropic elasticity theory, the strain energy W of a flexible chain with a Hamiltonian H is determined by using the same technique as for a chain treated as a random walk: given $H(\mathbf{r})$, the Green function $G(\mathbf{Q})$ is calculated from Eq. (11) and is normalized with the help of Eq. (12) to obtain the distribution function $p(\mathbf{Q})$. Afterwards, the strain energy $W(\mathbf{F})$ is determined by Eq. (6).

Two shortcomings of this approach should be mentioned: (i) for a chain with a Hamiltonian H, a correct measure of the free energy is the average Hamiltonian, while the use of Eqs. (6), (11) and

(12) appears to be unnecessary and questionable, and (ii) our previous analysis of a flexible chain grafted on a rigid surface demonstrates that the entropic elasticity theory leads to conclusions that contradict physical intuition [16].

In this study, we associate the free energy $\tilde{\Psi}(\mathbf{Q})$ of a chain with an end-to-end vector $\mathbf{Q}$ with the average Hamiltonian of this chain

$$\begin{aligned}\tilde{\Psi}(\mathbf{Q}) &= \langle H\rangle_{\mathbf{Q}} \\ &= \frac{1}{G(\mathbf{Q})}\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}} H(\mathbf{r}(s))\exp\Big(-\frac{H(\mathbf{r}(s))}{k_{\rm B}T}\Big)\mathcal{D}[\mathbf{r}(s)]. \end{aligned}\tag{13}$$

Given $\tilde{\Psi}(\mathbf{Q})$, we determine the normalized end-to-end distribution function $\tilde{p}(\mathbf{Q})$ from the equation similar to Eq. (4),

$$\tilde{p}(\mathbf{Q}) = \exp\Big(-\frac{\tilde{\Psi}(\mathbf{Q})}{k_BT}\Big)\Big[\int\exp\Big(-\frac{\tilde{\Psi}(\mathbf{Q})}{k_BT}\Big)d\mathbf{Q}\Big]^{-1},\tag{14}$$

and calculate the strain energy $\tilde{W}(\mathbf{F})$ as the average (over the distribution function) increment of free energy,

$$\tilde{W}(\mathbf{F}) = \int\Big[\tilde{\Psi}(\mathbf{F}\cdot\mathbf{Q}) - \tilde{\Psi}(\mathbf{Q})\Big]\tilde{p}(\mathbf{Q})d\mathbf{Q}.\tag{15}$$

Simple algebra reveals that for a Gaussian chain with Hamiltonian (1), our approach coincides with the conventional one and results in the strain energy density (9). However, for a flexible chain with excluded-volume interactions, Eqs. (13) to (15) differ from appropriate relations developed within the entropic elasticity theory.

An important remark regarding Eqs. (13) to (15) is that an additive constant in the expression for the free energy $\tilde{\Psi}(\mathbf{Q})$ does not affect the strain energy density $\tilde{W}(\mathbf{F})$ (as it is expected). This constant is excluded from the formula for the distribution function $\tilde{p}(\mathbf{Q})$ by the normalization condition (14), whereas it disappears in Eq. (15) because only the increment of free energy is substantial for the determination of $\tilde{W}(\mathbf{F})$.

3 Free energy of a chain with weak segment interactions

Our aim now is to calculate the free energy of a flexible chain with weak intra-chain interactions, Eqs. (2) and (3), in the first approximation with respect to the ratio v_0/k_BT. Inserting expressions (2) and (3) into Eq. (11), expanding the exponent into the Taylor series, and disregarding terms beyond the first order of smallness, we obtain

$$G(\mathbf{Q}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Big(1-\frac{\Phi(\mathbf{r}(s))}{k_BT}\Big)\exp\Big(-\frac{H_0(\mathbf{r}(s))}{k_{\rm B}T}\Big)\mathcal{D}[\mathbf{r}(s)] = \Big(1-\frac{\langle\Phi\rangle^0_{\mathbf{Q}}}{k_BT}\Big)G_0(\mathbf{Q}),\tag{16}$$

where $G_0(\mathbf{Q})$ is the Green function for a Gaussian chain, and the superscript index zero stands for averaging with the help of the Gaussian Hamiltonian. It follows from Eqs. (2), (3) and (13) that

$$\langle H\rangle_{\mathbf{Q}} = \frac{1}{G(\mathbf{Q})}\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Big(H_0(\mathbf{r}(s))+\Phi(\mathbf{r}(s))\Big)\exp\Big[-\frac{1}{k_{\rm B}T}\Big(H_0(\mathbf{r}(s))+\Phi(\mathbf{r}(s))\Big)\Big]\mathcal{D}[\mathbf{r}(s)].$$

Expanding the exponent into the Taylor series, using Eq. (16), and neglecting terms beyond the first order of smallness, we find that

$$\langle H\rangle_{\mathbf{Q}} = \Big(1+\frac{\langle\Phi\rangle^0_{\mathbf{Q}}}{k_BT}\Big)\frac{1}{G_0(\mathbf{Q})}\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Big(H_0(\mathbf{r}(s))+\Phi(\mathbf{r}(s))-\frac{1}{k_BT}H_0(\mathbf{r}(s))\Phi(\mathbf{r}(s))\Big)$$

$$
\begin{aligned}
& \times \exp\Big[-\frac{1}{k_{\rm B}T}H_0(\mathbf{r}(s))\Big]\mathcal{D}[\mathbf{r}(s)] \\
= & \Big(1+\frac{\langle\Phi\rangle^0_{\mathbf{Q}}}{k_BT}\Big)\Big(\langle H_0\rangle^0_{\mathbf{Q}}+\langle\Phi\rangle^0_{\mathbf{Q}}-\frac{1}{k_BT}\langle H_0\Phi\rangle^0_{\mathbf{Q}}\Big) \\
= & \langle H_0\rangle^0_{\mathbf{Q}}+\langle\Phi\rangle^0_{\mathbf{Q}}-\frac{1}{k_BT}\Big(\langle H_0\Phi\rangle^0_{\mathbf{Q}}-\langle H_0\rangle^0_{\mathbf{Q}}\langle\Phi\rangle^0_{\mathbf{Q}}\Big).
\end{aligned}
\tag{17}
$$

Our purpose now is to determine all terms on the right-hand side of Eq. (17) separately. To find the average of the Gaussian Hamiltonian $\langle H_0\rangle^0_{\mathbf{Q}}$, we insert expression (1) into Eq. (11) and introduce an explicit dependence of the Green function G_0 on segment length b_0

$$
G_0(b_0,\mathbf{Q})=\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big]\mathcal{D}[\mathbf{r}(s)]. \tag{18}
$$

Differentiation of Eq. (18) with respect to b_0 implies that

$$
\begin{aligned}
\frac{\partial G_0}{\partial b_0}(b_0,\mathbf{Q}) &= \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Big(\frac{3}{2b_0^2}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big)\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big]\mathcal{D}[\mathbf{r}(s)] \\
&= \frac{1}{k_BTb_0}\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}H_0(\mathbf{r}(s))\exp\Big[-\frac{H_0(\mathbf{r}(s))}{k_BT}\Big]\mathcal{D}[\mathbf{r}(s)] \\
&= \frac{1}{k_BTb_0}\langle H_0\rangle^0_{\mathbf{Q}}G_0(b_0,\mathbf{Q}).
\end{aligned}
$$

It follows from this relation that

$$
\langle H_0\rangle^0_{\mathbf{Q}}=\frac{k_BTb_0}{G_0(b_0,\mathbf{Q})}\frac{\partial G_0}{\partial b_0}(b_0,\mathbf{Q}). \tag{19}
$$

Substitution of expression (8) with $b^2=b_0L$ into Eq. (19) yields

$$
\langle H_0\rangle^0_{\mathbf{Q}}=\frac{3k_BT}{2}\Big(\frac{Q^2}{b^2}-1\Big). \tag{20}
$$

According to the definition of $\langle\Phi\rangle^0_{\mathbf{Q}}$ and Eq. (1), we have

$$
\langle\Phi\rangle^0_{\mathbf{Q}}G_0(b_0,\mathbf{Q})=\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Phi(\mathbf{r}(s))\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big]\mathcal{D}[\mathbf{r}(s)],
$$

where an explicit dependence of $\langle\Phi\rangle^0_{\mathbf{Q}}$ on b_0 is omitted for brevity. Differentiation of this equality with respect to b_0 results in

$$
\begin{aligned}
\frac{\partial}{\partial b_0}\Big(\langle\Phi\rangle^0_{\mathbf{Q}}G_0(b_0,\mathbf{Q})\Big) &= \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\Big(\frac{3}{2b_0^2}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big)\Phi(\mathbf{r}(s)) \\
&\quad\times\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2ds\Big]\mathcal{D}[\mathbf{r}(s)] \\
&= \frac{1}{k_BTb_0}\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}H_0(\mathbf{r}(s))\Phi(\mathbf{r}(s))\exp\Big[-\frac{H_0(\mathbf{r}(s))}{k_BT}\Big]\mathcal{D}[\mathbf{r}(s)] \\
&= \frac{1}{k_BTb_0}\langle H_0\Phi\rangle^0_{\mathbf{Q}}G_0(b_0,\mathbf{Q}).
\end{aligned}
\tag{21}
$$

It follows from Eq. (21) that

$$\begin{aligned}\langle H_0\Phi\rangle^0_{\mathbf{Q}} &= \frac{k_BTb_0}{G_0(b_0,\mathbf{Q})}\frac{\partial}{\partial b_0}\Big(\langle\Phi\rangle^0_{\mathbf{Q}}G_0(b_0,\mathbf{Q})\Big)\\ &= k_BTb_0\frac{\partial\langle\Phi\rangle^0_{\mathbf{Q}}}{\partial b_0}+\langle\Phi\rangle^0_{\mathbf{Q}}\frac{k_BTb_0}{G_0(b_0,\mathbf{Q})}\frac{\partial G_0}{\partial b_0}(b_0,\mathbf{Q}).\end{aligned}\tag{22}$$

Combination of Eqs. (19) and (22) implies that

$$\langle H_0\Phi\rangle^0_{\mathbf{Q}}-\langle H_0\rangle^0_{\mathbf{Q}}\langle\Phi\rangle^0_{\mathbf{Q}}=k_BTb_0\frac{\partial\langle\Phi\rangle^0_{\mathbf{Q}}}{\partial b_0}.\tag{23}$$

Inserting expressions (20) and (23) into Eq. (17), we arrive at the formula

$$\tilde{\Psi}(\mathbf{Q})=\frac{3k_BT}{2}\Big(\frac{Q^2}{b^2}-1\Big)+\langle\Phi\rangle^0_{\mathbf{Q}}-b_0\frac{\partial\langle\Phi\rangle^0_{\mathbf{Q}}}{\partial b_0}.\tag{24}$$

According to Eq. (24), to find the free energy of a flexible chain with weak segment interactions, we need to determine the energy of interactions averaged with respect to the Gaussian Hamiltonian $\langle\Phi\rangle^0_{\mathbf{Q}}$ only. To calculate this quantity, a perturbative technique is applied.

4 Correlation functions

Our aim now is to derive an explicit expression for the average of an exponential function of $\mathbf{r}(s)$ when the averaging is performed with respect to the Hamiltonian H_0. We begin with the perturbed Green function

$$\begin{aligned}G_0^{\mathbf{p}}(\mathbf{Q}) &= \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}}\exp\Big[-\frac{H_0(\mathbf{r}(s))}{k_{\rm B}T}+\int_0^L\mathbf{p}(s)\cdot\Big(\mathbf{r}(s)-\mathbf{r}^\circ(s)\Big)ds\Big]\mathcal{D}[\mathbf{r}(s)]\\ &= \langle\exp\Big(\int_0^L\mathbf{p}(s)\cdot\mathbf{r}'(s)ds\Big)\rangle^0_{\mathbf{Q}}G_0(\mathbf{Q}),\end{aligned}\tag{25}$$

where $\mathbf{p}(s)$ is a smooth vector function determined on $[0,L]$,

$$\mathbf{r}^\circ(s)=\mathbf{Q}\frac{s}{L}\tag{26}$$

is the "classical" path for a Gaussian chain, and

$$\mathbf{r}'(s)=\mathbf{r}(s)-\mathbf{r}^\circ(s).\tag{27}$$

Substitution of Eqs. (26) and (27) into Eqs. (11) and (25) results in

$$G_0^{\mathbf{p}}(\mathbf{Q})=\exp\Big(-\frac{3Q^2}{2b^2}\Big)\bar{G}^{\mathbf{p}}\mathbf{Q}),\qquad G_0(\mathbf{Q})=\exp\Big(-\frac{3Q^2}{2b^2}\Big)\bar{G}(\mathbf{Q}),\tag{28}$$

where

$$\begin{aligned}\bar{G}^{\mathbf{p}}(\mathbf{Q}) &= \int\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}'}{ds}(s)\Big)^2ds+\int_0^L\mathbf{p}(s)\cdot\mathbf{r}'(s)ds\Big]\mathcal{D}[\mathbf{r}'(s)],\\ \bar{G}(\mathbf{Q}) &= \int\exp\Big[-\frac{3}{2b_0}\int_0^L\Big(\frac{d\mathbf{r}'}{ds}(s)\Big)^2ds\Big]\mathcal{D}[\mathbf{r}'(s)],\end{aligned}\tag{29}$$

and the path integrals are calculated over all curves $\mathbf{r}'(s)$ that satisfy the boundary conditions

$$\mathbf{r}'(0) = \mathbf{r}'(L) = \mathbf{0}. \tag{30}$$

Setting

$$\mathbf{r}'(s) = \mathbf{r}_0(s) + \mathbf{R}(s), \tag{31}$$

where the functions $\mathbf{r}_0(s)$ and $\mathbf{R}(s)$ obey the zero boundary conditions

$$\mathbf{r}_0(0) = \mathbf{r}_0(L) = \mathbf{0}, \qquad \mathbf{R}(0) = \mathbf{R}(L) = \mathbf{0}. \tag{32}$$

we transform the expression in the square brackets in the first equality in Eq. (29) as follows:

$$\begin{aligned} A &\equiv -\frac{3}{2b_0}\int_0^L \Big(\frac{d\mathbf{r}'}{ds}(s)\Big)^2 ds + \int_0^L \mathbf{p}(s)\cdot\mathbf{r}'(s)ds \\ &= -\frac{3}{2b_0}\int_0^L \Big[\Big(\frac{d\mathbf{r}_0}{ds}(s)\Big)^2 + \Big(\frac{d\mathbf{R}}{ds}(s)\Big)^2 + 2\frac{d\mathbf{r}_0}{ds}(s)\cdot\frac{d\mathbf{R}}{ds}(s)\Big]ds \\ &\quad + \int_0^L \Big[\mathbf{p}(s)\cdot\mathbf{r}_0(s) + \mathbf{p}(s)\cdot\mathbf{R}(s)\Big]ds. \end{aligned} \tag{33}$$

Integration by parts with the use of Eq. (32) yields

$$\int_0^L \frac{d\mathbf{r}_0}{ds}(s)\cdot\frac{d\mathbf{R}}{ds}(s)ds = -\int_0^L \mathbf{r}_0(s)\cdot\frac{d^2\mathbf{R}}{ds^2}(s)ds.$$

It follows from this equality and Eq. (33) that

$$\begin{aligned} A &= -\frac{3}{2b_0}\int_0^L \Big[\Big(\frac{d\mathbf{r}_0}{ds}(s)\Big)^2 + \Big(\frac{d\mathbf{R}}{ds}(s)\Big)^2\Big]ds + \int_0^L \Big[\frac{3}{b_0}\frac{d^2\mathbf{R}}{ds^2}(s) + \mathbf{p}(s)\Big]\cdot\mathbf{r}_0(s)ds \\ &\quad + \int_0^L \mathbf{p}(s)\cdot\mathbf{R}(s)ds. \end{aligned}$$

Assuming the function $\mathbf{R}(s)$ to satisfy the differential equation

$$\frac{3}{b_0}\frac{d^2\mathbf{R}}{ds^2}(s) + \mathbf{p}(s) = 0, \tag{34}$$

we find that

$$A = -\frac{3}{2b_0}\int_0^L \Big[\Big(\frac{d\mathbf{r}_0}{ds}(s)\Big)^2 + \Big(\frac{d\mathbf{R}}{ds}(s)\Big)^2\Big]ds + \int_0^L \mathbf{p}(s)\cdot\mathbf{R}(s)ds. \tag{35}$$

The solution of Eq. (34) with boundary conditions (32) reads

$$\mathbf{R}(s) = \frac{b_0}{3}\int_0^L D(s,s')\mathbf{p}(s')ds', \tag{36}$$

where

$$D(s,s') = s'\Big(1-\frac{s}{L}\Big) \quad (s \ge s'), \qquad D(s,s') = s\Big(1-\frac{s'}{L}\Big) \quad (s \le s'). \tag{37}$$

Integrating by parts the second term in the square brackets in Eq. (35) and using Eqs. (32), (34) and (36), we obtain

$$\begin{aligned} \int_0^L \Big(\frac{d\mathbf{R}}{ds}(s)\Big)^2 ds &= -\int_0^L \mathbf{R}(s)\cdot\frac{d^2\mathbf{R}}{ds^2}(s)ds = \frac{b_0}{3}\int_0^L \mathbf{p}(s)\cdot\mathbf{R}(s)ds \\ &= \Big(\frac{b_0}{3}\Big)^2\int_0^L\int_0^L D(s,s')\mathbf{p}(s)\cdot\mathbf{p}(s')dsds'. \end{aligned}$$

Substitution of this expression and Eq. (36) into Eq. (35) results in

$$A = -\frac{3}{2b_0}\int_0^L \Big(\frac{d\mathbf{r}_0}{ds}(s)\Big)^2 ds + \frac{b_0}{6}\int_0^L\int_0^L D(s,s')\mathbf{p}(s)\cdot\mathbf{p}(s')ds ds'. \tag{38}$$

Bearing in mind that the last term in expression (38) can be taken away from the path integral, we conclude from Eqs. (28), (29) and (38) that

$$G_0^{\mathbf{p}}(\mathbf{Q}) = G_0(\mathbf{Q})\exp\Big[\frac{b_0}{6}\int_0^L\int_0^L D(s,s')\mathbf{p}(s)\cdot\mathbf{p}(s')ds ds'\Big].$$

Comparison of this equality with Eq. (25) implies that

$$\langle \exp\Big[\int_0^L \mathbf{p}(s)\cdot\mathbf{r}'(s)ds\Big]\rangle_{\mathbf{Q}}^0 = \exp\Big[\frac{b_0}{6}\int_0^L\int_0^L D(s,s')\mathbf{p}(s)\cdot\mathbf{p}(s')ds ds'\Big]. \tag{39}$$

Equation (39) serves as the basic tool for the analysis of correlations between the radius vectors $\mathbf{r}(s)$ at various points $s\in[0,L]$ of a chain. Setting

$$\mathbf{p}(s) = \mathbf{q}\delta(s-t_1) - \mathbf{q}\delta(s-t_2),$$

where $\mathbf{q}$ is an arbitrary vector, and $t_1, t_2 \in (0,L)$ are arbitrary points, we find from Eq. (39) that

$$\langle \exp\Big[\mathbf{q}\cdot\Big(\mathbf{r}'(t_1)-\mathbf{r}'(t_2)\Big)\Big]\rangle_{\mathbf{Q}}^0 = \exp\Big(\frac{b_0 q^2}{6}\Delta(t_1,t_2)\Big), \tag{40}$$

where

$$\Delta(t_1,t_2) = D(t_1,t_1) - 2D(t_1,t_2) + D(t_2,t_2). \tag{41}$$

In particular, when $\mathbf{q} = -\imath\mathbf{k}$, where $\imath=\sqrt{-1}$, and $\mathbf{k}$ is a real vector, Eq. (40) reads

$$\langle \exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}'(t_1)-\mathbf{r}'(t_2)\Big)\Big]\rangle_{\mathbf{Q}}^0 = \exp\Big(-\frac{b_0 k^2}{6}\Delta(t_1,t_2)\Big).$$

Replacing $\mathbf{r}'$ by $\mathbf{r}$ in accord with Eqs. (26) and (27), we obtain

$$\begin{aligned}\langle \exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}(t_2)-\mathbf{r}(t_1)\Big)\Big]\rangle_{\mathbf{Q}}^0 &= \langle \exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}'(t_1)-\mathbf{r}'(t_2)\Big)\Big]\rangle_{\mathbf{Q}}^0 \exp\Big(-\imath\mathbf{k}\cdot\mathbf{Q}\frac{t_2-t_1}{L}\Big)\\ &= \exp\Big(-\frac{b_0k^2}{6}\Delta(t_1,t_2) - \imath\mathbf{k}\cdot\mathbf{Q}\frac{t_2-t_1}{L}\Big).\end{aligned} \tag{42}$$

Our aim now is to apply Eq. (42) in order to calculate the average energy of segment interactions $\langle\Phi\rangle_{\mathbf{Q}}^0$ for the functional $\Phi(\mathbf{r})$ given by Eq. (3).

5 The average energy of segment interactions

We introduce the Fourier transform of the delta-function by the formula

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3}\int \exp(-\imath\mathbf{k}\cdot\mathbf{r})d\mathbf{k}, \tag{43}$$

combine Eqs. (3) and (43), and find that in a spherical coordinate frame $\{k,\phi,\theta\}$, whose $\mathbf{e}_3$ vector is directed along the end-to-end vector $\mathbf{Q}$, the functional Φ reads

$$\begin{aligned}\Phi(\mathbf{r}) &= \frac{v_0}{2L^2(2\pi)^3}\int_0^\infty k^2dk\int_0^{2\pi}d\phi\int_0^\pi\sin\theta d\theta\int_0^L ds\int_0^L \exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}(s)-\mathbf{r}(s')\Big)\Big]ds'\\ &= \frac{v_0}{L^2(2\pi)^3}\int_0^\infty k^2dk\int_0^{2\pi}d\phi\int_0^\pi\sin\theta d\theta\int_0^L ds\int_0^s \exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}(s)-\mathbf{r}(s')\Big)\Big]ds'.\end{aligned}$$

It follows from this relation and Eq. (42) that

$$\begin{aligned}\langle\Phi\rangle^0_{\mathbf{Q}} &= \frac{v_0}{L^2(2\pi)^3}\int_0^\infty k^2 dk \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^L ds \\ &\quad\times \int_0^s \exp\Bigl(-\frac{b_0 k^2}{6}\Delta(s,s') - \imath kQ\cos\theta \frac{s-s'}{L}\Bigr) ds'.\end{aligned}$$

Equations (37) and (41) imply that for any $s \geq s'$,

$$\Delta(s,s') = (s-s') - \frac{1}{L}(s-s')^2.$$

Using this equality, performing integration over ϕ, and setting $\tau = s - s'$, we obtain

$$\begin{aligned}\langle\Phi\rangle^0_{\mathbf{Q}} &= \frac{v_0}{(2\pi L)^2}\int_0^\infty k^2 dk \int_0^\pi \sin\theta d\theta \int_0^L ds \int_0^s \exp\Bigl[-\frac{b_0 k^2}{6}\Bigl(\tau - \frac{\tau^2}{L}\Bigr) - \imath kQ\cos\theta\frac{\tau}{L}\Bigr] d\tau \\ &= \frac{v_0}{(2\pi L)^2}\int_0^\infty k^2 dk \int_0^\pi \sin\theta d\theta \int_0^L (L-\tau)\exp\Bigl[-\frac{b_0 k^2}{6}\Bigl(\tau - \frac{\tau^2}{L}\Bigr) - \imath kQ\cos\theta\frac{\tau}{L}\Bigr] d\tau,\end{aligned}$$

where we changed the order of integration over s and τ and integrated over s explicitly. Introducing the notation $x = \cos\theta$ and $t = \tau/L$, we find that

$$\langle\Phi\rangle^0_{\mathbf{Q}} = \frac{v_0}{(2\pi)^2}\int_0^\infty k^2 dk \int_{-1}^1 dx \int_0^1 \exp\Bigl[-\frac{(bk)^2}{6}t(1-t) - \imath kQxt\Bigr](1-t)dt.$$

Bearing in mind that

$$\int_{-1}^1 \exp(-\imath kQxt)dx = \frac{2\sin(kQt)}{kQt},$$

we arrive at the formula

$$\langle\Phi\rangle^0_{\mathbf{Q}} = \frac{v_0}{2\pi^2}\int_0^\infty M_0(kQ,k)k^2 dk, \tag{44}$$

where

$$M_0(a,k) = \int_0^1 m(at)\exp\Bigl[-\frac{(bk)^2}{6}t(1-t)\Bigr](1-t)dt$$

and

$$m(x) = \frac{\sin x}{x}.$$

Differentiation of Eq. (44) with respect to b_0 implies that

$$b_0\frac{\partial\langle\Phi\rangle^0_{\mathbf{Q}}}{\partial b_0} = -\frac{v_0}{2\pi^2}\int_0^\infty M_1(kQ,k)k^2 dk, \tag{45}$$

where

$$M_1(a,k) = \frac{(bk)^2}{6}\int_0^1 m(at)\exp\Bigl[-\frac{(bk)^2}{6}t(1-t)\Bigr]t(1-t)^2 dt.$$

Substitution of expressions (44) and (45) into Eq. (24) yields

$$\tilde{\Psi}(\mathbf{Q}) = \frac{3k_B T}{2}\Bigl(\frac{Q^2}{b^2} - 1\Bigr) + \frac{v_0}{2\pi^2}\int_0^\infty M(kQ,k)k^2 dk, \tag{46}$$

where

$$M(a,k) = \int_0^1 m(at)\exp\Bigl[-\frac{(bk)^2}{6}t(1-t)\Bigr]\Bigl(1 + \frac{(bk)^2}{6}t(1-t)\Bigr)(1-t)dt.$$

Changing the order of integration in Eq. (46), we obtain

$$\tilde{\Psi}(\mathbf{Q}) = \frac{3k_BT}{2}\Big(\frac{Q^2}{b^2}-1\Big) + \frac{v_0}{2\pi^2 Q}\int_0^1 \frac{1-t}{t} J(t,Q)dt, \tag{47}$$

where

$$J(t,Q) = \int_0^\infty \exp\Big[-\frac{(bk)^2}{6}t(1-t)\Big]\Big(1+\frac{(bk)^2}{6}t(1-t)\Big)\sin(kQt)kdk.$$

Bearing in mind that the function under the integral is even, we present this equality in the form

$$J(t,Q) = \frac{1}{2}\int_{-\infty}^\infty \exp\Big[-\frac{(bk)^2}{6}t(1-t)\Big]\Big(1+\frac{(bk)^2}{6}t(1-t)\Big)\sin(kQt)kdk. \tag{48}$$

The integral in Eq. (48) is calculated with the help of the formulas

$$\int_{-\infty}^\infty \exp\Big(-\frac{\alpha k^2}{2}\Big)\sin(\beta k)kdk = \sqrt{\frac{2\pi}{\alpha}}\frac{\beta}{\alpha}\exp\Big(-\frac{\beta^2}{2\alpha}\Big),$$
$$\int_{-\infty}^\infty \exp\Big(-\frac{\alpha k^2}{2}\Big)\frac{\alpha k^2}{2}\sin(\beta k)kdk = \frac{1}{2}\sqrt{\frac{2\pi}{\alpha}}\frac{\beta}{\alpha}\exp\Big(-\frac{\beta^2}{2\alpha}\Big)\Big(3-\frac{\beta^2}{\alpha}\Big),$$

that are fulfilled for any $\alpha > 0$. Combination of these relations with Eq. (48) implies that

$$J(t,Q) = \frac{3Q\sqrt{6\pi}}{4b^3\sqrt{t(1-t)^3}}\Big(5-\frac{3Q^2t}{b^2(1-t)}\Big)\exp\Big(-\frac{3Q^2t}{2b^2(1-t)}\Big).$$

Inserting this expression into Eq. (47), we find that

$$\tilde{\Psi}(\mathbf{Q}) = \frac{3k_BT}{2}\Big[\Big(\frac{Q^2}{b^2}-1\Big) + \frac{v\sqrt{6\pi}}{4\pi^2b^3}\Big(5R_1(Q)-\frac{3Q^2}{b^2}R_2(Q)\Big)\Big], \tag{49}$$

where $v = v_0/(k_BT)$, and

$$\begin{aligned} R_1(Q) &= \int_0^1 \exp\Big(-\frac{3Q^2t}{2b^2(1-t)}\Big)\frac{dt}{\sqrt{t^3(1-t)}}, \\ R_2(Q) &= \int_0^1 \exp\Big(-\frac{3Q^2t}{2b^2(1-t)}\Big)\frac{dt}{\sqrt{t(1-t)^3}}. \end{aligned} \tag{50}$$

The function $R_2(Q)$ reads

$$\begin{aligned} R_2(Q) &= \int_0^\infty \exp\Big(-\frac{3Q^2\tau}{2b^2}\Big)\frac{d\tau}{\sqrt{\tau}} = 2\int_0^\infty \exp\Big(-\frac{3Q^2s^2}{2b^2}\Big)ds \\ &= \frac{2b}{Q\sqrt{3}}\int_0^\infty \exp\Big(-\frac{z^2}{2}\Big)dz = \frac{b}{Q}\sqrt{\frac{2\pi}{3}}, \end{aligned} \tag{51}$$

where we used the following variables: $\tau = t/(1-t)$, $s = \sqrt{\tau}$, and $z = Qs\sqrt{3}/b$. The first integral in Eq. (50) is presented in the form

$$R_1(Q) = R_0 - \int_0^1 \Big[1-\exp\Big(-\frac{3Q^2t}{2b^2(1-t)}\Big)\Big]\frac{dt}{\sqrt{t^3(1-t)}}, \tag{52}$$

where R_0 is independent of Q. According to the remark at the end of Section 2, the additive constant R_0 does not affect the increment of free energy $\Delta\tilde{\Psi}$ and the distribution function $\tilde{p}$, and

we do not calculate this quantity. Some concern may arise regarding R_0, because the integral in the formula for R_0 diverges. This divergence does not affect, however, the free energy. To avoid it, one can replace Eq. (43) for the delta-function by its regularization,

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3} \int U(k) \exp(-\imath \mathbf{k} \cdot \mathbf{r}) d\mathbf{k},$$

where

$$U(k) = 1 \quad (0 \le k \le k_*), \qquad U(k) = 0, \quad (k > k_*)$$

with some $k_* \gg 1$, find the free energy of a flexible chain with the regularized potential of segment interactions, disregard the additive constant in the expression for $\tilde{\Psi}(\mathbf{Q})$, and, afterwards, take the limit at $k_* \to \infty$. We do not dwell on detailed transformations, because they cause unnecessary complications of the analysis without influence on the final result.

The term dependent on Q in Eq. (52) is transformed as follows:

$$\begin{aligned} &\int_0^1 \Big[1 - \exp\Big(-\frac{3Q^2 t}{2b^2(1-t)} \Big) \Big] \frac{dt}{\sqrt{t^3(1-t)}} = \int_0^\infty \Big[1 - \exp\Big(-\frac{3Q^2 \tau}{2b^2} \Big) \Big] \tau^{-\frac{3}{2}} d\tau \\ &= \frac{Q}{b} \sqrt{\frac{3}{2}} \int_0^\infty \Big(1 - \exp(-s) \Big) s^{-\frac{3}{2}} ds, \end{aligned}$$

where we set $\tau = t/(1-t)$ and $s = 3Q^2\tau/(2b^2)$. Integration by parts results in

$$\int_0^\infty \Big(1 - \exp(-s) \Big) s^{-\frac{3}{2}} ds = 2 \int_0^\infty y^{-\frac{1}{2}} \exp(-y) dy = 2\Gamma(\frac{1}{2}) = 2\sqrt{\pi},$$

where $\Gamma(x)$ is the Euler gamma-function. Combining these relations, we find that

$$R_1(Q) = R_0 - \frac{Q}{b}\sqrt{6\pi}. \tag{53}$$

Substituting expressions (51) and (53) into Eq. (49) and neglecting additive constants, we arrive at the formula

$$\tilde{\Psi}(\mathbf{Q}) = \frac{3k_B T}{2} \Big(\frac{Q^2}{b^2} - \varepsilon \frac{Q}{b} \Big), \tag{54}$$

where

$$\varepsilon = \frac{9v}{\pi b^3}$$

is the dimensionless strength of excluded volume interactions. It follows from Eqs. (14) and (54) that

$$\tilde{p}(\mathbf{Q}) = p_0 \exp\Big[-\frac{3}{2} \Big(\frac{Q^2}{b^2} - \varepsilon \frac{Q}{b} \Big) \Big], \tag{55}$$

where the pre-factor p_0 is determined from the normalization condition

$$p_0 = \frac{1}{4\pi} \Big\{ \int_0^\infty \exp\Big[-\frac{3}{2} \Big(\frac{Q^2}{b^2} - \varepsilon \frac{Q}{b} \Big) \Big] Q^2 dQ \Big\}^{-1}. \tag{56}$$

For weak excluded-volume interactions ($\varepsilon \ll 1$), the integral in Eq. (56) is given by

$$\begin{aligned} \int_0^\infty \exp\Big[-\frac{3}{2} \Big(\frac{Q^2}{b^2} - \varepsilon \frac{Q}{b} \Big) \Big] Q^2 dQ &= \frac{b^3}{3\sqrt{3}} \Big[\int_0^\infty \exp\Big(-\frac{z^2}{2} \Big) z^2 dz + \frac{\varepsilon\sqrt{3}}{2} \int_0^\infty \Big(-\frac{z^2}{2} \Big) z^3 dz \Big] \\ &= \frac{b^3}{3\sqrt{3}} \Big(\sqrt{\frac{\pi}{2}} + \varepsilon\sqrt{3} \Big), \end{aligned}$$

where $z = Q\sqrt{3}/b$. This relation together with Eq. (56) implies that

$$p_0 = \Big(\frac{3}{2\pi b^2}\Big)^{\frac{3}{2}}\Big(1 - \varepsilon\sqrt{\frac{6}{\pi}}\Big) \tag{57}$$

in the first approximation with respect to ε. Inserting Eqs. (54) and (55) into Eq. (15) and introducing a spherical coordinate frame $\{Q, \phi, \theta\}$, we obtain

$$\begin{aligned}\tilde{W} &= \frac{3k_BTp_0}{2}\int_0^\infty \exp\Big[-\frac{3}{2}\Big(\frac{Q^2}{b^2} - \varepsilon\frac{Q}{b}\Big)\Big]Q^2dQ\int_0^{2\pi}d\phi \\ &\quad\times\int_0^\pi\Big[\frac{1}{b^2}\Big(\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q} - Q^2\Big) - \frac{\varepsilon}{b}\Big(\sqrt{\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q}} - Q\Big)\Big]\sin\theta d\theta.\end{aligned} \tag{58}$$

Denote by $\mathbf{i}_m$ the eigenvectors of the the right Cauchy–Green tensor $\mathbf{C}$ and by λ_m appropriate eigenvalues. If the $\mathbf{e}_3$ vector of the spherical coordinate frame is directed along the eigenvector $\mathbf{i}_3$, the expression $\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q}$ reads

$$\mathbf{Q}\cdot\mathbf{C}\cdot\mathbf{Q} = Q^2S, \qquad S = (\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)\sin^2\theta + \lambda_3\cos^2\theta.$$

Substitution of this relation into Eq. (58) results in

$$\tilde{W} = W_1 - W_2, \tag{59}$$

where

$$\begin{aligned}W_1 &= \frac{3k_BTp_0b^3}{2}\int_0^\infty \exp\Big[-\frac{3}{2}(z^2 - \varepsilon z)\Big]z^4dz\int_0^{2\pi}d\phi \\ &\quad\times\int_0^\pi\Big[\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)\sin^2\theta + \lambda_3\cos^2\theta\Big) - 1\Big]\sin\theta d\theta, \\ W_2 &= \frac{3\varepsilon k_BTp_0b^3}{2}\int_0^\infty \exp\Big[-\frac{3}{2}(z^2 - \varepsilon z)\Big]z^3dz\int_0^{2\pi}d\phi \\ &\quad\times\int_0^\pi\Big[\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)\sin^2\theta + \lambda_3\cos^2\theta\Big)^{\frac{1}{2}} - 1\Big]\sin\theta d\theta,\end{aligned}$$

and $z = Q/b$. We calculate the integrals over z, substitute expression (57) for the coefficient p_0, disregards terms beyond the first order of smallness with respect to ε, and find that

$$\begin{aligned}W_1 &= \frac{3k_BT}{8\pi}\Big(1 + \frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\int_0^{2\pi}d\phi\int_0^\pi\Big[\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)\sin^2\theta + \lambda_3\cos^2\theta\Big) - 1\Big]\sin\theta d\theta, \\ W_2 &= \frac{\varepsilon k_BT}{4\pi}\sqrt{\frac{6}{\pi}}\int_0^{2\pi}d\phi\int_0^\pi\Big[\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)\sin^2\theta + \lambda_3\cos^2\theta\Big)^{\frac{1}{2}} - 1\Big]\sin\theta d\theta.\end{aligned} \tag{60}$$

Calculating the integrals over ϕ and θ in the first equality in Eq. (60), we arrive at the formula

$$W_1 = \frac{k_BT}{2}\Big(1 + \frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)(\lambda_1 + \lambda_2 + \lambda_3 - 3). \tag{61}$$

According to Eqs. (9) and (61), at $\varepsilon = 0$ (no intra-chain interactions), W_1 coincides with the strain energy of a Gaussian chain. Setting $x = \cos\theta$ in the other equality in Eq. (60) and using the evenness of the function under the integral, we find that

$$\begin{aligned}W_2 &= \frac{\varepsilon k_BT}{2\pi}\sqrt{\frac{6}{\pi}}\int_0^{2\pi}d\phi\int_0^1\Big[\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)(1 - x^2) + \lambda_3x^2\Big)^{\frac{1}{2}} - 1\Big]dx \\ &= \varepsilon k_BT\sqrt{\frac{6}{\pi}}\Big[\frac{1}{2\pi}\int_0^{2\pi}d\phi\int_0^1\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)(1 - x^2) + \lambda_3x^2\Big)^{\frac{1}{2}}dx - 1\Big] \\ &= \varepsilon k_BT\sqrt{\frac{6}{\pi}}\Big[\frac{2}{\pi}\int_0^{\frac{\pi}{2}}d\phi\int_0^1\Big((\lambda_1\cos^2\phi + \lambda_2\sin^2\phi)(1 - x^2) + \lambda_3x^2\Big)^{\frac{1}{2}}dx - 1\Big].\end{aligned} \tag{62}$$

Although it is possible to develop an analytical expression for the strain energy W_2 for an arbitrary three-dimensional deformation, an appropriate formula is rather cumbersome, and we do not present it for the sake of brevity. We confine ourselves to a particular case of axisymmetric deformation with

$$\lambda_1 = \lambda_2 = \lambda \tag{63}$$

for two reasons: (i) under condition (63) the governing relations remain relatively simple, and (ii) deformation processes (63) are typical for experiments on uniaxial and equi-biaxial extension of elastomers. Performing integration over ϕ in Eq. (62), we obtain

$$W_2 = \varepsilon k_B T \sqrt{\frac{6}{\pi}} \Big[\int_0^1 \Big(\lambda + (\lambda_3 - \lambda) x^2 \Big)^{\frac{1}{2}} dx - 1 \Big].$$

Calculation of the integral over x implies that

$$\begin{aligned}
W_2 &= \frac{\varepsilon k_B T}{2} \sqrt{\frac{6}{\pi}} \Big(\sqrt{\lambda_3} + \frac{\lambda}{\sqrt{\lambda_3 - \lambda}} \ln \frac{\sqrt{\lambda_3} + \sqrt{\lambda_3 - \lambda}}{\sqrt{\lambda}} - 2 \Big) \quad (\lambda_3 > \lambda), \\
W_2 &= \frac{\varepsilon k_B T}{2} \sqrt{\frac{6}{\pi}} \Big(\sqrt{\lambda_3} + \frac{\lambda}{\sqrt{\lambda - \lambda_3}} \arcsin \sqrt{\frac{\lambda - \lambda_3}{\lambda}} - 2 \Big) \quad (\lambda_3 < \lambda), \\
W_2 &= \varepsilon k_B T \sqrt{\frac{6}{\pi}} \Big(\sqrt{\lambda_3} - 1 \Big) \quad (\lambda_3 = \lambda).
\end{aligned} \tag{64}$$

To obtain the strain energy W_2 as a function of the principal stretches λ_m, the parameter λ in Eq. (64) should be replaced by $\frac{1}{2}(\lambda_1 + \lambda_2)$.

6 Constitutive equations for a network of flexible chains

To develop stress–strain relations for a permanent network of flexible chains with excluded volume interactions, we adopt the following hypotheses: (i) the motion of chains is affine, which means that the deformation gradient $\mathbf{F}$ coincides with the deformation gradient for macro-deformation, and (ii) inter-chain interactions are accounted for by using the incompressibility condition, which implies that the strain energy of a network equals the sum of strain energies of individual chains [13]. Denote by M the number of chains per unit volume. It follows from Eqs. (59), (61) and (62) that the strain energy density (per unit volume of the network) reads

$$\begin{aligned}
\bar{W}(\lambda_m) &= \frac{k_B T M}{2} \Big\{ \Big(1 + \frac{\varepsilon}{3} \sqrt{\frac{6}{\pi}} \Big) (\lambda_1 + \lambda_2 + \lambda_3 - 3) \\
&\quad - 2\varepsilon \sqrt{\frac{6}{\pi}} \Big[\frac{2}{\pi} \int_0^{\frac{\pi}{2}} d\phi \int_0^1 \Big((\lambda_1 \cos^2\phi + \lambda_2 \sin^2\phi)(1 - x^2) + \lambda_3 x^2 \Big)^{\frac{1}{2}} dx - 1 \Big] \Big\}.
\end{aligned} \tag{65}$$

The principal Cauchy stresses Σ_m are expressed in terms of the strain energy $\bar{W}$ as [14]

$$\Sigma_m = -P + \lambda_m \frac{\partial \bar{W}}{\partial \lambda_m}, \tag{66}$$

where P stands for pressure. Formulas (65) and (66) provide the stress–strain relations for an incompressible network of flexible chains with weak excluded-volume interactions.

Our aim now is to apply these equations in order to evaluate the effect of segment interactions on the elastic response of a polymer network at uniaxial tension (compression) and equi-biaxial tension.

6.1 Uniaxial tension

Uniaxial tension of an incompressible medium is described by the formulas

$$x_1 = k^{-\frac{1}{2}} X_1, \qquad x_2 = k^{-\frac{1}{2}} X_2, \qquad x_3 = k X_3,$$

where $\{X_m\}$ and $\{x_m\}$ are Cartesian coordinates in the reference and actual states, respectively, and k denotes elongation ratio. The right Cauchy–Green tensor $\mathbf{C}$ is given by

$$\mathbf{C} = k^{-1}(\mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2) + k^2 \mathbf{e}_3\mathbf{e}_3,$$

where $\mathbf{e}_m$ are base vectors of the Cartesian frame in the initial state, and its eigenvalues read

$$\lambda_1 = \lambda_2 = k^{-1}, \qquad \lambda_3 = k^2. \tag{67}$$

Inserting expressions (67) into Eq. (65) and using Eq. (64), we find that

$$\begin{aligned} \bar{W} &= \frac{k_B T M}{2}\Big[\Big(1+\frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(k^2+\frac{2}{k}-3\Big) - \varepsilon\sqrt{\frac{6}{\pi}}\Big(k + \frac{\ln(\sqrt{k^3}+\sqrt{k^3-1})}{\sqrt{k(k^3-1)}} - 2\Big)\Big] \qquad (k>1), \\ \bar{W} &= \frac{k_B T M}{2}\Big[\Big(1+\frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(k^2+\frac{2}{k}-3\Big) - \varepsilon\sqrt{\frac{6}{\pi}}\Big(k + \frac{\arcsin\sqrt{1-k^3}}{\sqrt{k(1-k^3)}} - 2\Big)\Big] \qquad (k<1). \end{aligned} \tag{68}$$

According to Eq. (66), at uniaxial tension (compression) the longitudinal Cauchy stress Σ is determined as

$$\Sigma = \lambda_3 \frac{\partial \bar{W}}{\partial \lambda_3} - \lambda_1 \frac{\partial \bar{W}}{\partial \lambda_1} = \lambda_3 \frac{\partial \bar{W}}{\partial \lambda_3} - \frac{1}{2}\lambda_1 \frac{\partial \bar{W}}{\partial \lambda}.$$

Substitution of expressions (67) into this equality yields

$$\Sigma = k \frac{d\bar{W}}{dk},$$

which implies that the engineering tensile stress $\sigma = \Sigma/k$ is given by

$$\sigma = \frac{d\bar{W}}{dk}. \tag{69}$$

Combination of Eqs. (68) and (69) implies that

$$\begin{aligned} \sigma &= k_B T M\Big[\Big(1+\frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(k-\frac{1}{k^2}\Big) \\ &\quad -\frac{\varepsilon}{2}\sqrt{\frac{6}{\pi}}\Big(1+\frac{3\sqrt{k^3(k^3-1)}-(4k^3-1)\ln(\sqrt{k^3}+\sqrt{k^3-1})}{2\sqrt{k^3(k^3-1)^3}}\Big)\Big] \qquad (k>1), \\ \sigma &= k_B T M\Big[\Big(1+\frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(k-\frac{1}{k^2}\Big) - \frac{\varepsilon}{2}\sqrt{\frac{6}{\pi}} \\ &\quad \times\Big(1-\frac{3\sqrt{k^3(1-k^3)}+(1-4k^3)\arcsin\sqrt{1-k^3}}{2\sqrt{k^3(1-k^3)^3}}\Big)\Big] \qquad (k<1). \end{aligned} \tag{70}$$

It is easy to check that $\lim_{k\to 1}\sigma(k) = 0$, which means that the reference state is stress-free. Differentiation of the first equality in Eq. (70) with respect to k yields

$$\begin{aligned} \frac{d\sigma}{dk} &= k_B T M\Big\{\Big(1+\frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(1+\frac{2}{k^3}\Big) - \frac{3\varepsilon}{8k^{\frac{5}{2}}}\sqrt{\frac{6}{\pi}} \\ &\quad \times \frac{1}{(k^3-1)^{\frac{5}{2}}}\Big[(8k^6+1)\ln(\sqrt{k^3}+\sqrt{k^3-1}) - (10k^3-1)\sqrt{k^3(k^3-1)}\Big]\Big\}. \end{aligned} \tag{71}$$

The Young's modulus of a network is defined as

$$E = \frac{d\sigma}{dk}\Big|_{k=1}.$$

Inserting expression (71) into this equality and applying the L'Hospital rule to calculate the limit at $k \to 1$, we find that

$$E = E_0\Big(1 + \frac{\varepsilon}{15}\sqrt{\frac{6}{\pi}}\Big), \tag{72}$$

where

$$E_0 = 3k_B TM$$

stands for the Young's modulus of a network of Gaussian chains. According to Eq. (72), excluded-volume interactions induce an increase in the elastic modulus of a network of flexible chains which is proportional to the dimensionless strength of segment interactions ε.

To assess the effect of intra-chain interactions on the stress–strain diagrams, we perform numerical simulation of Eqs. (70) at uniaxial tension and compression. The results of numerical analysis are presented in Figures 1 (tension) and 2 (compression), where the reduced tensile stress

$$\sigma_* = \frac{\sigma_0}{k - k^{-2}},$$

is depicted versus elongation ratio k (the Mooney–Rivlin plots). Here $\sigma_0 = \sigma/(k_B TM)$ stands for the dimensionless engineering tensile stress. In these figures, the functions $\sigma_*(k)$ for a network of Gaussian chains are presented by horizontal lines, whereas appropriate dependencies for a network of flexible chains with segment interactions demonstrate a monotonic increase in tensile and compressive stresses (it is worth noting that a weak minimum of σ_* at compression observed in Figure 2 does not reflect non-monotonicity of the dependence $\sigma(k)$; the latter function decreases with k in the entire domain $k \in (0, 1)$). The results plotted in Figures 1 and 2 indicate that excluded-volume interactions cause the growth of stiffness of a polymer network, in agreement with Eq. (72) that determines the elastic modulus at small strains.

Our aim now is to assess the influence of segment interactions on the mechanical response of an incompressible polymer network at equi-biaxial tension.

6.2 Equi-biaxial tension

Equi-biaxial tension of an incompressible material is described by the formulas

$$x_1 = kX_1, \qquad x_2 = kX_2, \qquad x_3 = k^{-2}X_3,$$

where k stands for elongation ratio. The right Cauchy–Green tensor reads

$$\mathbf{C} = k^2(\mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2) + k^{-4}\mathbf{e}_3\mathbf{e}_3,$$

and its eigenvalues are given by

$$\lambda_1 = \lambda_2 = k^2, \qquad \lambda_3 = k^{-4}. \tag{73}$$

As equi-biaxial tests on an incompressible layer are conventionally performed in the tensile mode, we confine ourselves to the case $k > 1$. Substituting expressions (73) into Eqs. (65) and using Eq. (64), we find that

$$\bar{W} = \frac{k_B TM}{2}\Big[\Big(1 + \frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(2k^2 + \frac{1}{k^4} - 3\Big) - \varepsilon\sqrt{\frac{6}{\pi}}\Big(\frac{1}{k^2} + \frac{k^4}{\sqrt{k^6-1}}\arcsin\frac{\sqrt{k^6-1}}{k^3} - 2\Big)\Big]. \tag{74}$$

According to Eqs. (66), the Cauchy tensile stress Σ is determined by the formula

$$\Sigma = \frac{1}{2}\lambda_1 \frac{\partial \bar{W}}{\partial \lambda} - \lambda_3 \frac{\partial \bar{W}}{\partial \lambda_3} = \frac{k}{2}\frac{d\bar{W}}{dk}.$$

It follows from this relation that the engineering tensile stress $\sigma = \Sigma/k$ reads

$$\sigma = \frac{1}{2}\frac{d\bar{W}}{dk}. \tag{75}$$

Substitution of expression (74) into Eq. (75) results in

$$\sigma = k_B T M \Big\{ \Big(1 + \frac{\varepsilon}{3}\sqrt{\frac{6}{\pi}}\Big)\Big(k - \frac{1}{k^5}\Big) + \frac{\varepsilon}{4}\sqrt{\frac{6}{\pi}}\Big[\frac{2}{k^3} - \frac{k^3}{k^6 - 1}\Big(\frac{k^6 - 4}{\sqrt{k^6 - 1}} \arcsin \frac{\sqrt{k^6 - 1}}{k^3} + 3\Big)\Big]\Big\}. \tag{76}$$

It follows from Eq. (76) that $\lim_{k\to 1} \sigma(k) = 0$, which means that the initial state is stress-free.

The dependence of the dimensionless tensile stress σ_0 on elongation ratio k is depicted in Figure 3 for $\varepsilon = 0$ (a network of Gaussian chains) and $\varepsilon = 0.5$ (a network of flexible chains with excluded-volume interactions). This figure shows that segment interactions induce an increase in the tensile stress at all elongation ratios k. The difference between tensile stresses monotonically grows with k. At $k = 6.0$ (which is in the range of deformations reached in experiments on elastomers), the engineering stress in a network of chains with segment interactions exceeds that in a network of Gaussian chains by 28%.

The results of numerical simulation at uniaxial tension of an incompressible medium are also presented in Figure 3 for comparison. According to this figure, at relatively large elongation ratios ($k > 3.0$), the difference between the tensile stresses (corresponding to these two deformation modes) in a Gaussian network disappears, whereas an appropriate difference in a network of flexible chains with excluded-volume interactions remains quite pronounced. Although under both deformation programs, excluded-volume interactions induce an increase in stiffness of the network, the effect of segment interactions on the stress–strain relation is stronger at equi-biaxial tension than at uniaxial tension.

7 Concluding remarks

The concept of non-entropic elasticity is proposed for the analysis of the mechanical response of a network of flexible chains with excluded-volume interactions. Unlike the classical theory of entropic elasticity, where the free energy of a chain is entirely characterized by the distribution function of end-to-end vectors, we associate the free energy of a chain with the average value of its Hamiltonian. The average free energy of a chain and the strain energy density of a network are calculated explicitly (under the assumption that the strength of excluded-volume interactions is small compared with thermal energy). Constitutive equations are developed for a network of macromolecules with intra-chain interactions under an arbitrary three-dimensional deformation. These relations are simplified for uniaxial tension (compression) and equi-biaxial tension of an incompressible medium at finite strains. An explicit expression is derived for the elastic modulus of a network of chains with weak segment interactions. The effect of intra-chain interactions on the stress–strain diagram is analyzed numerically. It is demonstrated that excluded-volume interactions result in an increase in the tensile stress at both deformation modes under consideration. This growth is substantial (about 30% at elongations typical for experiments on rubbers), which means that the account for excluded-volume interactions is quite important for applications.

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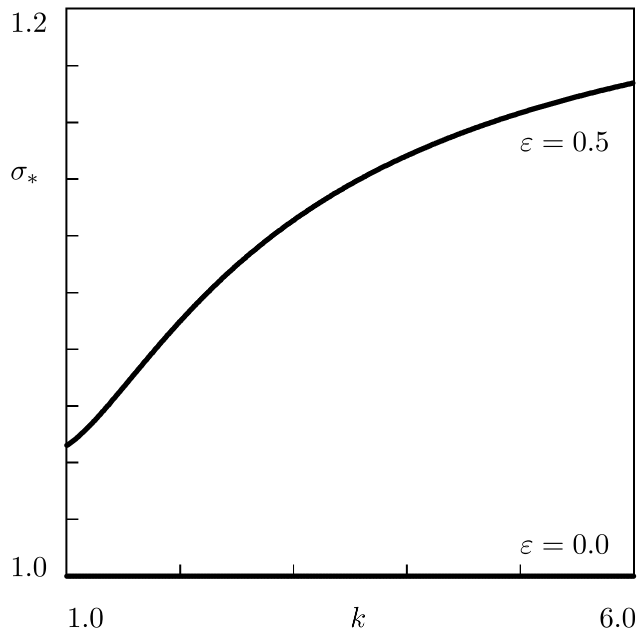

Figure 1:

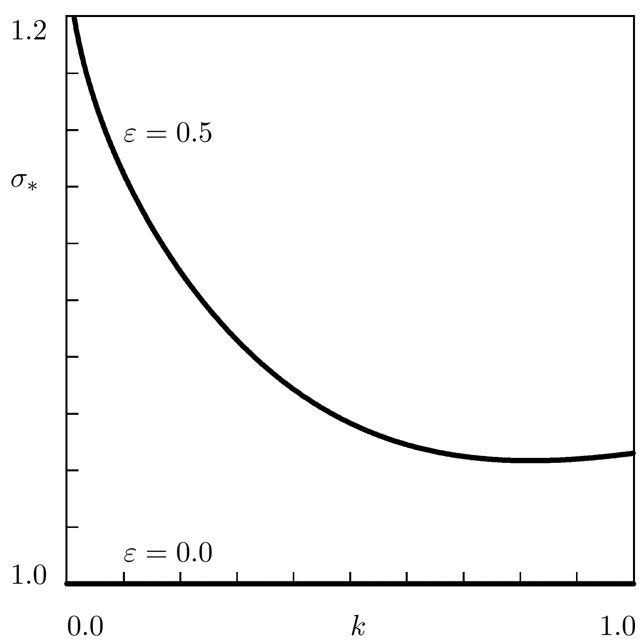

Figure 2:

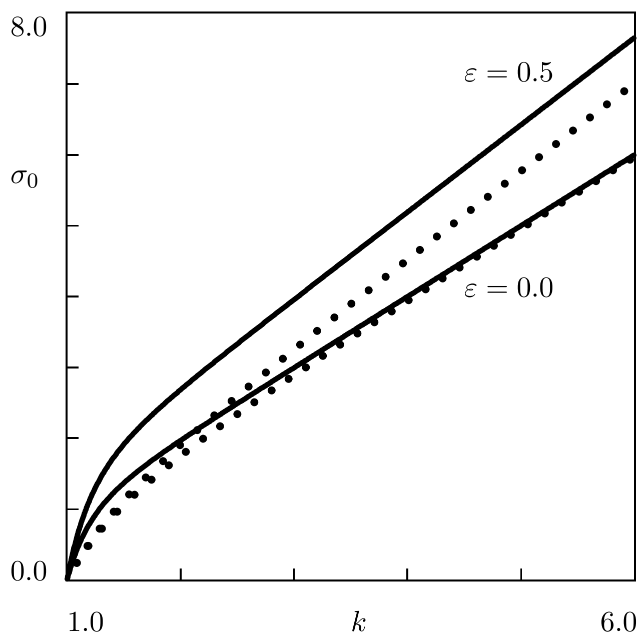

Figure 3: